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Abstract

The ternary nitride La_2GaN_3 was synthesized from the elements and an excess of sodium and gallium at 900°C in a sealed niobium tube. La_2GaN_3 is yellow colored and crystallizes with the Ba_2ZnO_3 structure [monoclinic space group *C*2/c (No.15), a = 5.6709(5) Å, b = 10.945(1) Å, c = 11.986(1) Å, β = 93.591(5)°, V = 742.54(12) Å^3, Z = 8] and is isostructural with the $A_2^{II}M^{V}N_3$ nitrides, $Sr(Ba)_2TaN_3$, $Sr(Ba)_2NbN_3$, $Ca(Sr)_2VN_3$. The structure contains infinite chains of GaN_4 tetrahedral anions, $^1_\infty[GaN_2N_{2/2}]^{6-}$.

1. Introduction

Binary nitrides of the main group elements, such as GaN, Si_3N_4, and AlN, are technologically of interest. Especially gallium nitride is a key material for blue/ultraviolet light emitting diodes (LEDs) and lasers as well as for sensors for UV-light. The synthesis of new nitrides is thus a field of growing interest in solid-state chemistry in the search for new materials with promising properties and applications. However, very little is presently known about multinary gallium nitrides. DiSalvo et al. have reported several compounds with nitridogallate anions in the past ten years which often show novel structures. For example, Sr_3GaN_3 and Sr_6GaN_5 contain isolated planar $[GaN_3]^{6-}$ anions [1], $Sr_3Ga_2N_4$ [2] and $Ba_3Ga_2N_4$ [3] contain edge-shared $[GaN_{4/2}]^{3-}$ tetrahedra, while α-$Ca_3Ga_2N_4$ and $Sr_3Ga_3N_5$ [2] and the recently reported quaternary nitride $LiCaGaN_2$ [4] exhibit structures based on corner-shared $[Ga_2N_6]$ dimers which are formed by two edge-sharing tetrahedra. Let us finally note the two compounds β-$Ca_3Ga_2N_4$ [5] and $LiSrGaN_2$ [6] have structures that are based on interpenetrating networks. The anti-perovskite compound Nd_3GaN has been mentioned in the literature and is the only reported compound in a rare-earth/gallium/nitrogen system but it cannot be described in terms of anionic nitridometalate species and fully oxidized cations as the nitrogen atoms are not bonded to gallium atoms in the structure [7].

Here we report the synthesis and the crystal structure of the first reported rare-earth nitridogallate compound, La_2GaN_3 that contains infinite chains of corner-sharing $[GaN_2N_{2/2}]^{6-}$ tetrahedra.

2. Experimental

Clear yellow and air stable crystals of La_2GaN_3 were first observed as a by-product while investigating the ternary lanthanum-tungsten-nitrogen system using an excess of sodium and gallium as a flux. The compound was further successfully synthesized from a tungsten-free reaction as described in the following procedure. Due to the air sensitivity of the reagents, all manipulations were carried out in an argon-filled glove box. Na, Ga, La and NaN_3 were placed into a niobium tube (OD ≈ 1 cm, length ≈ 12 cm) in the atomic ratios of Na:Ga:La:N_2 were 6:4:1:3. The corresponding masses are Na (Aldrich, A.C.S reagent grade) 83 mg, Ga (99.99%) 200 mg, La (filled from rod, Jonhson Matthey Company) 100 mg and NaN3 (99.9%) 47 mg. The niobium container was sealed under argon in a Centorr Associates arc furnace and then itself sealed under vacuum in a fused silica tube in order to protect it from subsequent oxidation during heating. The silica tube was then placed into a muffle furnace, heated up to 900°C in 15 h, held at temperature for 36 h. Then the furnace was allowed to cool to RT over 100 h. Following this heating sequence, the niobium tube was opened and unreacted sodium was removed by evaporation from the products by heating the niobium tube to 350°C under a pressure of ~ 10^{-6} bar for 8h.

The products of the reaction were analyzed with powder X-ray diffraction using a Scintag 2000 θ-θ diffractometer with Cu$K\alpha$ radiation. The sample was prepared in an argon-filled glove box and covered with Mylar film to prevent reaction with air and moisture. Single crystal X-ray diffraction data were obtained using a Brucker X8 Apex II diffractometer equipped with 4K CCD detector and graphite monochromatized Mo$K\alpha$ radiation (λ = 0.07107 Å). The Brucker software package SAINT [8] was used

to integrate the data, an empirical absorption correction was applied using SADABS [9] and the initial input files for solving the structure prepared by XPREP [10]. The integrated data were analyzed with the SHELX97 [11] suite of programs within WinGX [12]. The La:Ga ratio of La_2GaN_3 was determined by standardless electron microprobe analysis performed with a JEOL 8900 electron microprobe.

3. Results and Discussion

After the sodium was removed from the sample, the tube was moved back into the argon-filled glove box. The remaining product appeared as a dark gray, silvery mass in which no crystals were clearly visible by eye. A fraction of the product was ground in an agate mortar for powder X-ray diffraction analysis but only LaN, Na_xGa_y and La_xGa_y phases could be identified. Another portion of the reaction product was placed into polybutene oil for inspection under an optical microscope. Small sized clear yellow and air stable crystals were apparent with two distinct shapes: block crystals and thin long plates. Several of them were analyzed and all were consistent with a monoclinic symmetry independent of the shape of the selected crystal. A suitable crystal with approximate 80*60*60 μm^3 dimensions was chosen for data collection. Its structure was solved in *C*2/c (No. 15). Details of the refinement are shown in Table 1. No extra symmetry was found by ADDSYM [12]. The atomic coordinates were standardized with STRUCTURE TIDY [13] and are shown in Table 2. The anisotropic displacement factors are detailed in Table 3. In order to verify the elemental composition found by the single crystal XRD solution, semi-quantitative electron microprobe spectroscopy measurement were carried out. Results were similar for the

two different shapes of crystal and revealed a La:Ga ratio of 1.9:1. These data are within the expected errors for a standardless measurement. No signal corresponding to sodium, gallium or niobium were observed. The presence of nitrogen was confirmed by wavelength dispersive spectroscopy.

La_2GaN_3 crystallizes with the Ba_2ZnO_3 structure (Fig. 1) [14] and is isostructural to the $A_2^{II}M^{V}N_3$ nitrides: $Ca(Sr)_2VN_3$ [15, 16], $Sr(Ba)_2NbN_3$ [17, 18] and $Sr(Ba)_2TaN_3$ [19, 20]. The structure is built up by La^{3+} cations and nitridogallate anions which form parallel infinite chains of vertex-linked $[GaN_3]^{4-}$ group along [100] with a pattern that repeats after two tetrahedra (Fig. 2). One characteristic of those chains is the difference between Ga–N4–Ga and Ga–N1–Ga angle values, i.e. 176.6° and 111.1°, where N4 and N1 are the bridging nitrogen. Such chains can be described after Liebau [21] as "zweier single chains" and the chain torsion angle can be defined by N1–N4–N1 in La_2GaN_3 with a value of 135.2°. By comparison, the chain angle in isostructural Ba_2ZnO_3 is 139.9°, and the $Zn–O_{bridging}–Zn$ angles are 178.3° and 115.3°. The monoclinic distortion in La_2GaN_3 ($\beta = 93.59°$) is similar to that of Ba_2ZnO_3 ($\beta = 93.63°$) but larger than the ones observed in the $A^{II}{}_2M^{V}N_3$ series where $90.99° < \beta < 92.34°$. The average distances of gallium to bridging nitrogen and terminal nitrogen are 1.936 Å and 1.983 Å respectively. Those distances are slightly shorter than the ones observed in the ternary nitrides $A_3Ga_2N_4$ (A = Sr, Ba) that contain infinite edge sharing chains $^{1}_{\infty}[GaN_{4/2}]^{3-}$, i.e. 2.005 Å and 2.017 Å respectively for Sr and Ba [2, 3]. The La^{3+} are coordinated to seven nitrogen atoms with distances ranging from 2.45 Å to 3.22 Å (Table 4). La(1) is coordinated to nitrogen in a monocapped trigonal prismatic geometry while for La(2) a distorted pentagonal bipyramid is observed (Fig. 2). The average La–N bond length is ~ 2.70 Å, comparable to that reported in the binary nitride

LaN (~ 2.65 Å) or in the lanthanum-containing ternary nitrides of the $RE_3M_2N_6$ family where RE = rare earth element and M = V (~ 2.68 Å) [22], Nb (~ 2.73 Å), Ta (~ 2.63 Å) [23] or Cr (~ 2.63 Å) [24].

4. Conclusion

The new nitride La_2GaN_3 has been synthesized and is the first reported ternary compound in a rare-earth/gallium/nitrogen system which can be described in terms of anionic nitridometalate species and fully oxidized cations. It crystallizes in the Ba_2ZnO_3 structure-type.

5. Acknowledgment

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Figures and tables captions

Figure 1: Structure of La_2GaN_3 showing the arrangement of the corner sharing tetrahedral $^{1}_{\infty}[GaN_2N_{2/2}]^{4-}$ chains.

Figure 2: Depiction of the $^{1}_{\infty}[GaN_2N_{2/2}]^{4-}$ chains and coordination polyhedrons of La in La_2GaN_3.

Table 1: Crystal data and structure refinement for La_2GaN_3.

Table 2: Atomic coordinates and values of U_{eq}, the equivalent isotropic displacement parameter ($Å^2$ x 10^3), for La_2GaN_3.

Table 3:Anisotripic displacement parameters ($Å^2$ x 10^3) for La_2GaN_3.

Table 4: Selected bond lengths for La_2GaN_3 (Å) .

Figure 1

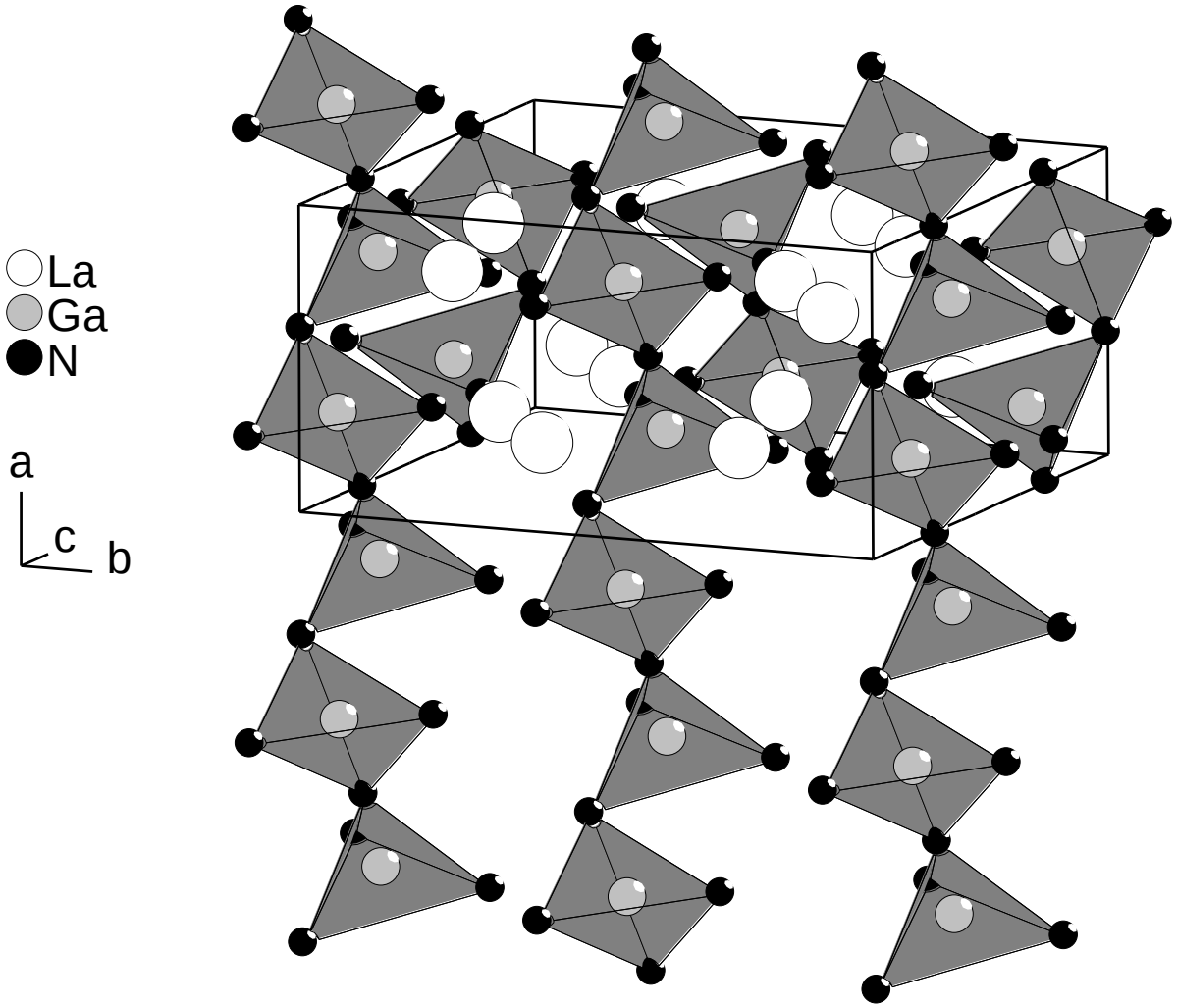

Figure 2

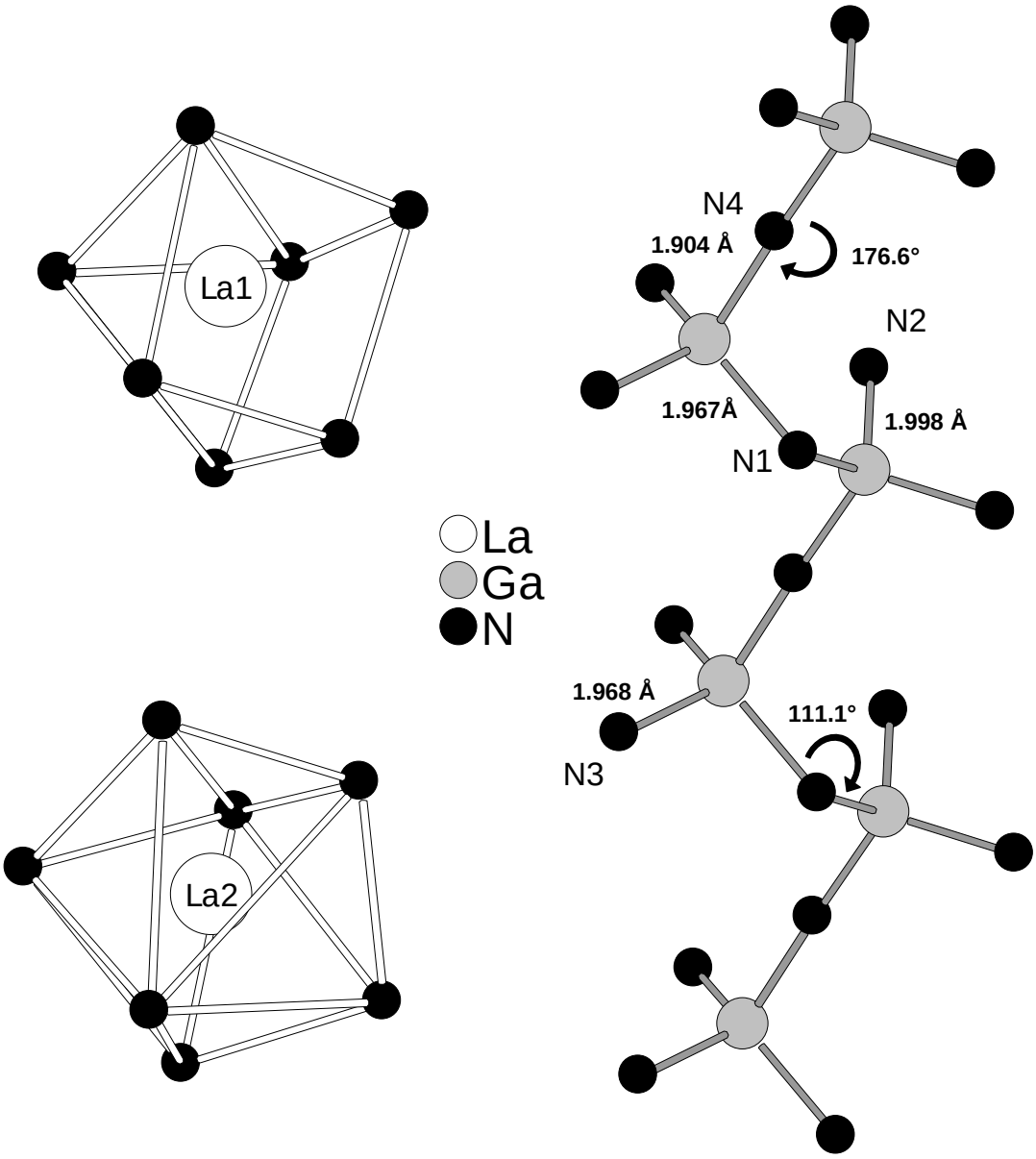

Table 1

Empirical formula	La_2GaN_3
Formula weight (*M*)	389.57
Temperature (K)	167(2)
Crystal system	Monoclinic
Space group	*C*2/c
a (Å)	5.6709(5)
b (Å)	10.945(1)
c (Å)	11.986(1)
β (°)	93.591(5)
Volume ($Å^3$)	742.54(12)
Z	8
Density (calculated) ($Mg\ m^{-3}$)	6.970
Absorption coefficient (μ) (mm^{-1})	29.584
Reflections collected	6330
Independent reflections	1843 [R_{int} = 0.0251]
Goodness-of-fir on F^2	1.014
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.029
	w*R*2 = 0.0401
R indices (all data)	*R*1 = 0.0273
	w*R*2 = 0.0410

Table 2

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq}
La1	8*f*	0.2385(1)	0.2074(1)	0.3488(1)	4(1)
La2	8*f*	0.2585(1)	0.3945(1)	0.0744(1)	4(1)
Ga	8*f*	0.2993(1)	0.0016(1)	0.1629(1)	3(1)
N1	4*e*	0	0.4000(3)	0.25	5(1)
N2	8*f*	0.3220(5)	0.1783(3)	0.1305(2)	6(1)
N3	8*f*	0.2222(5)	0.1002(2)	0.5280(2)	7(1)
N4	4*e*	0	0.0068(4)	0.25	8(1)

U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La1	4(1)	3(1)	4(1)	0(1)	0(1)	0(1)
La2	4(1)	3(1)	3(1)	0(1)	0(1)	0(1)
Ga	3(1)	3(1)	3(1)	0(1)	0(1)	0(1)
N1	6(2)	4(2)	5(2)	0	-2(1)	0
N2	6(1)	4(1)	7(1)	1(1)	1(1)	-2(1)
N3	8(1)	5(1)	7(1)	0(1)	0(1)	0(1)
N4	7(2)	11(2)	6(2)	0	0(1)	0

The anisotropic displacement factor takes the form $-2\pi^2[h^2a^{*2}U^{11} + \cdots + 2hka^*b^*U^{12}]$

Table 4

La1—N1	2.734(3)
La1—N2	2.509(3), 2.707(3), 3.220(3)
La1—N3	2. 454(3), 2.574(3)
La1—N4	2.802(3)
La2—N1	2.640(1)
La2—N2	2.480(3), 2.595(3)
La2—N3	2.569(3), 2.722(3), 3.058(1)
La2—N4	2.730(2)
Ga—N1	1.967(2)
Ga—N2	1.998(3)
Ga—N3	1.968(3)
Ga—N4	1.904(1)